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Test Procedure for Gross Alpha Particle Activity in Drinking Water Interlaboratory Collaborative Study

Lockheed Engineering and Management Services Co., Inc.
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TEST PROCEDURE FOR GROSS ALPHA PARTICLE ACTIVITY IN DRINKING WATER
Interlaboratory Collaborative Study

by

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Contract Number 68-03-3249

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16. ABSTRACT

A new test procedure for measuring the concentration of gross alpha particle activity in drinking water samples was multilaboratory tested with 18 laboratories in a collaborative study. Gross alpha activity values were calculated with four different alpha emitting radionuclide standard counting efficiencies to see which standard was best for gross alpha activity determinations. Thorium-230, a pure alpha emitter, appeared to be the best standard for gross alpha counting efficiency. A secondary purpose in this study was to see how well the Ra-226 concentration of a drinking water sample could be estimated from an early gross alpha count (three hours after separation) subtracted from a late gross alpha count (seven days after separation) and calculated from the equation provided in the test procedure. The method for gross alpha particle concentration measurement eliminates the dissolved solids interference problem (which is a significant problem for the EPA approved method) and provides for greater sensitivity by allowing for the use of much larger samples in the analysis.

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ABSTRACT

A new test procedure for measuring the concentration of gross alpha particle activity in drinking water samples was multilaboratory tested with 18 laboratories in a collaborative study. Gross alpha activity values were calculated with four different alpha emitting radionuclide standard counting efficiencies to see which standard was best for gross alpha activity determinations. Thorium-230, a pure alpha emitter, appeared to be the best standard for gross alpha counting efficiency.

Water samples A, B, C, and D contained gross alpha concentrations of 74.0 pCi/L, 52.6 pCi/L, 4.8 pCi/L, and 10.0 pCi/L, respectively, at three hours after separation of the alpha emitting radionuclides from the water by coprecipitation with iron hydroxide and barium sulfate. A statistical analysis of the test results from the 18 laboratories, using the Th-230 counting efficiency, showed coefficients of variation for repeatability (within-laboratory precision) of 7.9 percent, 7.8 percent, 8.7 percent, and 8.8 percent, respectively, for an average of 8.3 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.4 percent, 16.8 percent, 18.7 percent, and 18.5 percent, respectively, for an average of 18.6 percent.

A comparison of the 18 laboratory grand average results (calculated with the Th-230 counting efficiency) with the known gross alpha particle concentrations showed accuracy indexes of 91.9 percent, 99.4 percent, 122 percent, and 94.5 percent, respectively, for an average accuracy index of 102 percent. The t-test to show significant difference applied to the data showed a significant bias (+) for sample C but no significant bias for the other three samples.

A secondary purpose in this study was to see how well the Ra-226 concentration of a drinking water sample could be estimated from an early gross alpha count (three hours after separation) subtracted from a late gross alpha count (seven days after separation) and calculated from the equation provided in the test procedure.

Water samples A, B, C, and D contained Ra-226 concentrations of 47.2 pCi/L, 20.5 pCi/L, 3.0 pCi/L, and 0.0 pCi/L, respectively. A statistical analysis of the test results from the 18 laboratories (17 laboratories for sample C) showed coefficients of variation for repeatability (within-laboratory precision) of 8.2 percent, 9.5 percent, and 14.8 percent for samples A, B, and C, respectively, for an average of 10.8 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.5 percent, 25.8 percent, and 23.8 percent, respectively, for an average of 23.4 percent.

A comparison of the 18 laboratory (17 laboratories for sample C) grand average results with the known Ra-226 concentrations showed accuracy indexes of 98.3 percent, 102 percent, and 96.7 percent, respectively for samples A, B, and C, for an average of 99.0 percent. The t-test to show significant differences applied to the data showed no significant bias in the method.

This method for gross alpha particle concentration measurement eliminates the dissolved solids interference problem (which is a significant problem for the EPA approved method) and provides for greater sensitivity by allowing for the use of much larger samples in the analysis. It is recommended that the method be accepted as a validated method for gross alpha activity in drinking water. It is further recommended that the method be accepted as a valid method for the estimation of Ra-226 concentrations in drinking water.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM	-- the American Society for Testing and Materials
EPA	-- Environmental Protection Agency
NIPDWR	-- National Interim Primary Drinking Water Regulations
c/m or cpm	-- counts per minute
d/m or dpm	-- disintegrations per minute
pCi/L	-- picocuries per liter
pCi/mL	-- picocuries per milliliter
Am-241	-- americium-241
Ra-226	-- radium-226
Th-230	-- thorium-230
U	-- uranium
Po-210	-- polonium-210
mg	-- milligram (0.001 gram)
cpm/pCi	-- counts per minute per picocurie
cpm/dpm	-- counts per minute per disintegrations per minute
$16\underline{M}HNO_3$	-- 16 molar nitric acid
mm	-- millimeter
conc.	-- concentrated
H_2SO_4	-- sulfuric acid
$BaCl_2 \cdot 2H_2O$	-- barium chloride hydrate
$Fe(NO_3)_3 \cdot 9H_2O$	-- ferric nitrate hydrate
NH_4OH	-- ammonium hydroxide

SYMBOLS

2S%	-- two sigma percent (two standard deviations in percent)
A_j%	-- the accuracy index for the sample j
n	-- the number of replicate analyses
p	-- the number of participant laboratories in the study
S_{ij}	-- the standard deviation of the replicate test results for sample j by lab i
S_{rj}	-- the repeatability (within-laboratory) standard deviation for sample j
S_{Lj}	-- the standard deviation of between-laboratories precision for sample j
S_{Rj}	-- the reproducibility (combined within- and between-laboratory) standard deviation for sample j
$S_{\bar{x}j}$	-- the standard deviation of the grand average for sample j
V_{rj}%	-- the coefficient of variation for repeatability (within-laboratory) for sample j
V_{Lj}	-- the coefficient of variation for bewteen-laboratories precision for sample j

V_{R_j} -- the coefficient of variation for reproducibility (combined within- and between-laboratory) for sample j

$\bar{X}_j$ -- the grand average value for sample j

Y_j -- the known value of the sample j concentration (pCi/L)

$\bar{X}_{ij}$ -- the arithmetic average of all replicate test results of sample j by lab i

X_{ijh} -- the test result of replicate h of sample j by lab i

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SECTION 1

INTRODUCTION

The National Interim Primary Drinking Water Regulations (NIPDWR) require a gross alpha activity measurement of all public drinking water supplies as a screening determination of the presence of alpha emitting radionuclides. The need for specific radionuclide analysis of water supplies is therefore dictated by the gross alpha activity test results of those supplies.

Alpha emitting radionuclides are not separated from the dissolved solids of the sample in the Environmental Protection Agency (EPA) approved test procedures for gross alpha activity (Kreiger 1976, 1980). An aliquot of the sample is simply evaporated to dryness, and the residue is counted for alpha activity. Drinking water supplies vary widely in dissolved solids concentrations (from less than 100 mg per liter to over 5,000 mg per liter). The recommended maximum evaporated dissolved solids residue in a 2-inch diameter counting dish is 100 mg (5 mg per square centimeter) because of the sample residue self-absorption of the alpha particles. For drinking water supplies with dissolved solids greater than 500 mg per liter, the approved test procedure for gross alpha activity measurement is limited because of the small sample aliquots that can be analyzed and because of the very long counting times that are necessary to meet the required sensitivity of measurement (3 pCi/liter) (EPA 1976).

A new test procedure for gross alpha activity was reported by Robert Lieberman of the EPA Eastern Environmental Research Facility (EERF) at the 1982 Health Physics Meeting in Las Vegas, Nevada. The new procedure (see Appendix B of the Project Report) coprecipitates all alpha emitting actinides with barium sulfate and iron hydroxide carriers and thereby separates the alpha emitting actinides from other sample dissolved solids. Larger sample aliquots can be analyzed so that the alpha measurement sensitivity is improved, and the necessary counting time is minimized.

This new procedure, "Test Procedure for Gross Alpha Particle Activity in Drinking Water by Coprecipitation," has been tested by 18 laboratories in a collaborative study, and the results are described in this report.

A major purpose for gross alpha activity measurements of all public water supplies has been to screen those supplies for a potential Radium-226 health hazard to the public. A secondary purpose in this study was to determine how well an estimate of the Radium-226 content of a water sample could be made by an early and by a late count of the gross alpha activity after separation from the water sample.

Precision, accuracy, and bias statements are made in this report for both

gross alpha activity measurements and for the estimated Radium-226 content of each sample.

The study was conducted by the author while employed at the EPA Environmental Monitoring Systems Laboratory at Las Vegas, Nevada, and the calculations and reporting of that study was done as an employee of Lockheed Engineering and Management Co., Inc. (LEMSCO), under Contract No. 68-03-3249, Task 70.12.

SECTION 2

CONCLUSIONS

The problem of high dissolved solids in gross alpha activity measurements of drinking water samples is eliminated by this test procedure. This test procedure also provides for increased sensitivity over the approved method by allowing for the use of larger sample aliquots in gross alpha measurements.

The physical instability of iron hydroxide precipitate when dried on a filter (especially a membrane filter) without the aid of a holding agent can result in loss of precipitate, contamination of the alpha counting system, and poor reproducibility of the test procedure. The problem would be intolerable when samples are to be counted in a windowless gas flow proportional counting system (still used by some laboratories). The coprecipitate is physically more stable on glass fiber filters than on membrane filters because the surface glass fibers act as a holding agent to some extent. However, the addition of as little as 5 mg of paper pulp fiber to the sample aliquot can hold the co-precipitate even on membrane filters well enough to appear physically stable when dry. The test procedure was modified to include the use of paper pulp fibers to secure the precipitate to the filter.

There have been many discussions for many years about which alpha emitting radionuclide is the best standard for a gross alpha counting efficiency. This study will probably not end those discussions, but it may provide information on which to base the setting of a standard for the amended (or revised) drinking water regulations.

The public health would be better served by a gross alpha measurement with a high bias than one with a low bias and would, therefore, require a more specific measurement of a potential health hazard. For all 18 laboratories, americium-241 gave higher counting efficiencies than the 3 other standards and, therefore, also gave lower gross alpha activity measurements (biased low for 3 of the 4 samples). The uranium counting efficiency gave sample test results that were biased slightly high for three of the four samples. The thorium-230 counting efficiency gave test results with no significant low or high bias for three of the four samples, but sample C was biased high. Thorium-230 appears to be the best choice for a standard for gross alpha activity measurements.

The coprecipitate weights reported by the laboratories for standard calibration samples and for the water samples show more consistency within each laboratory than do the alpha count data. This indicates that coprecipitate recoveries were quite consistent within each laboratory and that they do not account for the differences in the alpha count data. The differences in co-precipitate weights between laboratories and also between samples within each

laboratory are very likely due to the differences in the weights of the paper pulp pellets and to the differences in the paper pulp amounts in the portions of paper pulp suspension solution added to each standard and water sample.

Since the standard calibration samples were taken through the same analytical steps as the water samples, the coprecipitate recovery factors are combined in the factor that is labeled as the counting efficiency.

The difference in alpha activity between a late count (seven days after separation) and an early count (three hours after separation) can be used to estimate the radium-226 concentration of a water sample with quite good accuracy. The presence of uranium and polonium-210 in some of the samples did not bias the radium-226 estimates.

Laboratories were instructed to use their own tap water to prepare the samples. Therefore, there was probably quite a bit a variability in the sample dissolved solids. This did not seem to be a factor in either the gross alpha activity measurements or in the estimation of the radium-226 in the samples.

The repeatability precision (within-laboratory precision), reproducibility percision (the combined within- and between-laboratory precision), the accuracy, and the bias have been determined for the test procedure by a multilaboratory study. These have been determined for gross alpha activity measurements and for the estimation of Ra-226 in drinking water.

Precision, accuracy, and bias statements are made here for the gross alpha activity values as determined with the Th-230 counting efficiency. Similar statements can be made for the gross alpha activity values as determined by the counting efficiencies of the other three standards.

The estimated repeatability (within-laboratory) precisions of the test procedure for the determination of gross alpha particle concentrations at the 74.0 pCi/L (sample A) level (18 participant average) is 10.8 pCi/L (2S% = 14.6%); at the 52.6 pCi/L (sample B) level (18 participant average) is 8.2 pCi/L (2S% = 15.6%); at the 4.8 pCi/L (sample C) level (18 participant average) is 1.0 pCi/L (2S% = 21.2%); and at the 10.0 pCi/L (sample D) level (18 participant average) is 1.6 pCi/L (2S% = 16.6%).

The estimated reproducibility (combined within- and between) precision of the test procedure for the determination of gross alpha particle concentrations at the 74.0 pCi/L (sample A) level (18 lab average) is 27.8 pCi/L (2S% = 37.5%); at the 52.6 pCi/L (sample B) level (18 lab average) is 17.6 pCi/L (2S% = 33.5%); at the 4.8 pCi/L (sample C) level (18 lab average) is 2.2 pCi/L (2S% = 45.8%); and at the 10.0 pCi/L (sample D) level (17 lab average) is 3.5 pCi/L (2S% = 35.0%).

The accuracy indexes for the gross alpha particle concentration measurements for the four water samples A, B, C, and D are 91.9 percent, 99.4 percent, 122 percent, and 94.5 percent, respectively, for an average accuracy index of 102 ± 11.9 percent. Bias (percent) values for the samples are -8.1 percent, -0.6 percent, +22.3 percent, and -5.5 percent, respectively.

For the estimation of Ra-226 concentrations in water samples by the Appendix C method of the test procedure, the estimated repeatability (within-laboratory) precision at the 47.2 pCi/L (sample A) level (18 lab average) is 7.6 pCi/L (2S% = 16.1%); at the 20.5 pCi/L (sample B) level (18 lab average) is 4.0 pCi/L (2S% = 19.5%); and at the 3.0 pCi/L (sample C) level (17 lab average) is 0.86 pCi/L (2S% = 28.7%). Sample D contained no Ra-226. The early and later gross alpha count of sample D by the participating laboratories revealed no Ra-226 in sample D.

The accuracy indices for samples A, B, and C, are 98.3 percent, 102 percent, and 96.7 percent, respectively, for an average accuracy index for the method of 99.0 ± 2.2 percent. The bias (percent) values for the samples are -1.7 percent, +1.9 percent, and -3.3 percent, respectively.

Radium-224 is a possible but not a likely interference in the estimation of Ra-226 concentration of a drinking water sample from a two-count gross alpha measurement (Appendix D). At equal concentrations of Ra-224 and Ra-226 (Ra-224/Ra-226 = 1) and with the Ra-224 being supported by its parent progeny Ra-228 and Th-228, the estimation of the Ra-226 concentration will be biased high by about 40 percent. At a concentration ratio equal to 0.5 (Ra-224/Ra-226 = 0.5), the bias will be about 18 percent; and at a concentration ratio equal to 2 (Ra-224/Ra-226 = 2), the bias will be about 81 percent. However, Radium-224 is not a likely interference because the geochemistry of thorium tends to make Th-228 more sedimentary than soluble. Also, since Ra-228 with its progeny is now believed to be at least as much as a hazard to public health as is Ra-226, a high estimate of the Ra-226 concentration of a drinking water sample because of a Ra-224 interference would be in the interest of public health. Appendix D gives Ra-224 interference calculations based upon theoretical calculations and not upon analytical tests.

SECTION 3

RECOMMENDATIONS

It is recommeded that the method tested procedure (Appendix B) be considered a valid alternate test procedure for the determination of gross alpha particle activity in drinking water.

It is recommeded that this test procedure be considered a valid method for the determination of Radium-226 in drinking water.

It is recommeded that thorium-230 be used as the standard for determining the gross alpha activity counting efficiency. Standard solutions of thorium-230 are available from the Quality Assurance Division of EMSL-Las Vegas. If standard solutions of thorium-230 become unavailable, it is recommended that natural uranium be used as a gross alpha activity standard.

SECTION 4

EXPERIMENTAL PROCEDURES

ANALYTICAL TEST PROCEDURE

The analytical test procedure used in this study is described in detail in Appendix B. The procedure is capable of quantifying drinking water gross alpha particle activity and of providing for an accurate estimate of the Radium-226 in drinking water supplies.

COLLABORATIVE TEST PROCEDURES

Standard Solutions

An ampoule of each standard solution (Am-241, Ra-226, Th-230, and uranium) was sent to each participating laboratory for counting efficiency determinations by this test procedure. Instructions to the participants listed the standard radionuclide concentrations. See Appendix C for instructions to the participating laboratories.

Sample Solutions

Four ampoules containing sample concentrate solutions were sent to each participating laboratory. Detailed instructions for sample concentrate dilutions were sent to each participating laboratory (Appendix C) and included report sheets and ingrowth tables. Table 7 of this report shows the known radionuclide concentrations for the diluted samples.

General Procedures

A total 28 laboratories agreed to participate in the collaborative test of the test procedure, and 18 laboratories submitted their test results. All the laboratories that submitted results are listed in Appendix A.

DATA PROCESSING PROCEDURES

The data from the 18 participant laboratories were tested for outliers by the ASTM recommeded criterion for rejection (ASTM 1980). When a particular laboratory test result was in question, the T value was calculated by Equation 1.

$$T_n = (X_n - \overline{X})/S \qquad (1)$$
$$T_1 = (X_1 - \overline{X})/S,$$

where: $T_{nj}T_i$ = test criterion

$\bar{X}$ = arithmetic average of all n values
S = the estimate of the population standard deviation based on the sample data.

If T_n or T_1 values exceeded the critical values, the measurement in question was rejected. Critical values of T for a 5 percent, two-sided level of significance were used for the rejection criterion.

A statistical evaluation of the test results was carried out by the procedures described in E-691, E-177, and E-178 of the ASTM Standard Part 41, 1980. The standard deviations and other statistical parameters and equations for their calculations are listed below. The standard deviation of individual participant (or laboratory) test results, S_{ij}, was determined by Equation 2.

$$S_{ij} = \left[\sum_{h=1}^{n_{ij}} (X_{ijh} - \bar{X}_{ij})^2/(n_{ij} - 1) \right]^{1/2} \quad (2)$$

where: X_{ijh} = the result reported for the h replicate of the j sample material by lab i
$\bar{X}_{ij}$ = the mean of the individual results for sample j for lab i
n_{ij} = the number of replicates reported for sample j by lab i

The repeatability (within-laboratory) standard deviation, Srj, for each sample was determined by Equation 3 and 3A.

Where the number of replicates was the same (3) for all participants, Equation 3 was used.

$$S_{r_j} = \left(1/P \sum_{i=1}^{P} S_{ij}^2 \right)^{1/2} \quad (3)$$

where: P = the number of participants in the study.

Where the number of replicates were not the same for all participants, Equation 3A was used.

$$S_{r_j} = \left[\frac{\sum_{i=1}^{P} [(n_{ij} - 1)\, S_{ij}^2]}{\sum_{i=1}^{P} (n_{ij} - 1)} \right]^{1/2} \quad (3A)$$

The standard deviation of the grand average for each sample $S_{\bar{x}_j}$, was determined by Equation 4.

$$S_{\bar{x}_j} = \left[\sum_{i=1}^{P} (\bar{X}_{ij} - \bar{X}_j)^2/(P-1) \right]^{1/2} \quad (4)$$

where: $\bar{X}_{ij}$ = the average of the test results for sample material j by lab i

$\bar{X}_j$ = the grand average for sample material j

The standard deviation of between-laboratory precision for each sample material, S_L , was determined by Equation 5.

$$S_{L_j} = \left(S_{\bar{x}_j}^2 - \frac{S_{x_j}^2}{n} \right)^{1/2} \quad (5)$$

The reproducibility (combined within- and between-laboratory) standard deviation for each sample, S_{R_j}, was determined by Equation 6.

$$S_{R_j} = \left(S_{r_j}^2 + S_{L_j}^2 \right)^{1/2} \quad (6)$$

The coefficient of variation for repeatability (within-laboratory for each sample $V_{r_j}\%$, was determined by Equation 7.

$$V_{r_j}\% = 100\, S_{r_j}/\bar{x}_j \quad (7)$$

The coefficient of variation for between-laboratory precision for each sample, $V_{L_j}\%$, was determined by Equation 8.

$$V_{L_j}\% = 100\, S_{L_j}/\bar{x}_j \quad (8)$$

The coefficient of variation for reproducibility (combined within- and between laboratory) for each sample, $V_{R_j}\%$, was determined by Equation 9.

$$V_{R_j}\% = 100\, S_{R_j}/\bar{x}_j \quad (9)$$

The accuracy index, $A_j\%$, a percent relationship of the grand average, X_j, to the known value, Y_j, for each sample material was determined by Equation 10.

$$A_j\% = 100\, \frac{\bar{X}_j}{Y_j} \quad (10)$$

Bias, the difference between the known value and the measured mean value, was determined by Equation 11.

$$\text{Bias} = Y - \overline{X}_j \tag{11}$$

where

Y = The known value.

Percent Bias was determined by Equation 12.

$$\% \text{ Bias} = \frac{Y - \overline{X}_j}{Y} \times 100 \tag{12}$$

A comparison of the grand average value, X_j, with the known value, Y_j, for each sample in a bias test was determined by Equation 13 (Youden and Steiner, 1975).

$$t_j = \frac{\bar{X}_j - Y_j}{S_{\bar{X}j}/(P)^{1/2}}, \text{ (P-1) degrees of freedom} \tag{13}$$

where t_j = the bias test result for the j sample
P = the number of participants

SECTION 5

RESULTS AND DISCUSSIONS

Table 1 lists the individual laboratory average coprecipitate weights for the four standard calibration samples (averages of three replicate sample portions). Table 2 lists the individual laboratory average coprecipitate weights for the four water samples (average of three replicate sample portions). The paper pulp pellets sent to the participating laboratories for use in this study varied slightly in weight. Therefore, the coprecipitate weights for both standards and water samples are consistently the same for each laboratory, but they differ somewhat between the laboratories. Two of the labortories (No. 1 and No. 14) apparently used more paper pulp of iron and barium carrier than the other 15 laboratories. One laboratory did not submit weights. However, the coprecipitate recovery precision within each laboratory looked good.

Tables 3 through 6 list individual laboratory averages of three replicate analyses for gross alpha activity of water samples A through D as determined by four different radionuclide standard counting efficiencies. The standard deviations of each laboratory average are listed. Grand averages and their standard deviations are given for gross alpha activity as calculated by using the four different radionuclide standard counting efficiencies.

Gross alpha activity measurements for water samples A, B, and D as determined with the Am-241 standard counting efficiency show a definite low bias. Gross alpha measurements for all four water samples as determined with the Ra-226 or Th-230 standard counting efficiency are within one standard deviation of the known value. As determined with the uranium standard counting efficiency, the gross alpha grand average is well within one standard deviation of the known values for samples A, B, and D and is within two standard deviations of the known value for sample C. Thorium-230 appears to be the best standard for the gross alpha counting efficiency.

Table 7 lists the radionuclide known value concentrations of the four water samples and the gross alpha activity grand averages as determined by the four different radionuclide standard counting efficiencies. These were put in the same table for an easier look at any correlations between the gross alpha measured values from the various standard counting efficiencies and the sample radionuclide content. There does not appear to be any correlation.

Tables 8 through 11 lists the precision, accuracy, and bias values for the 4 water samples for gross alpha activity measurements as determined by the 4 different standard counting efficiencies. The t-test to show significant differences between the known value and the grand average value was conducted for all four samples measured by the four standard counting efficiencies. For

sample C, all four values are significantly different from the known value for gross alpha activity. For samples A and D, gross alpha activity values as measured with the Th-230 and uranium standards counting efficiencies are not significantly different from the known values. Values determined with the Am-241 and Ra-226 standard counting efficiencies are significantly different from the known values. For sample B, gross alpha activity values determined with the Ra-226, Th-230, and uranium standard counting efficiencies are not significantly different from the known value. Values determined with the Am-241 standard counting efficiency are significantly different from the known value.

Table 12 lists the estimated Ra-226 concentration of the 4 water samples as determined from an early gross alpha count (3 hours after separation) subtracted from a late gross alpha count (7 days after separation) and calculated by the equation provided in Appendix C of the test procedure. The counting efficiency (cpm/pCi) for the Ra-226 estimation was calculated from the following equation:

$$\frac{\text{Late Alpha count cpm - Early Alpha count cpm}}{\text{Ingrowth factor x Ra-226 pCi/L}} = \text{cpm/pCi/L}$$

For seven days ingrowth, the factor is 2.1538.

The author neglected to provide a column on the data report sheets for the calibration standard samples for gross alpha counts. Participants simply calculated and reported their counting efficiencies (cpm/pCi). However, some of the laboratories apparently reported cpm/dpm values in the cpm/pCi column. Where this was obvious, the author called participants for the gross alpha count of the standards and then recalculated the counting efficiencies.

By using known Ra-226 concentrations of the four water samples and the participating laboratory early and late gross alpha counts, average counting efficiencies (cpm/pCi) were calculated for each laboratory. Then the estimated Ra-226 concentrations were calculated by using the equation in Appendix C of the test procedure. That data is listed in Table 13, which is not significantly different than the data in Table 12.

Tables 14 and 15 also list estimated Ra-226 concentration values for the water samples. Counting efficiencies for Table 14 calculations were determined by early and late gross alpha counts of Ra-226 standard calibration samples and by the known gross alpha pCi values for those water samples. The following equation was used for those counting efficiencies:

$$\frac{\text{Late Alpha count cpm - Early Alpha count cpm}}{\text{Late Alpha pCi - Early Alpha pCi}} = \text{cpm/pCi}$$

If the early and late alpha counts are made at about the same time after separation for water samples as for calibration standard samples, this calculation for the counting efficiency should be valid. The early count should be 3 to 24 hours after separation, and the late count should be about one week after separation.

Precision and bias calculations were not done for the data in Tables 13, 14, and 15 because the grand averages of those tables are not significantly different from the corresponding grand averages in Table 12.

Table 16 gives the precision, accuracy, and bias values for the estimated water sample Ra-226 concentrations reported in Table 12. The t-test was conducted to show signficant differences between the grand averages and the known values. There were no significant differences between the grand averages of the estimated Radium-226 values for the four water samples and the known values. In fact, the estimated values appear to be good enough to be specifically measured values.

TABLE 1. COPRECIPITATE WEIGHTS FOR STANDARD SAMPLES

Laboratory	Standard sample coprecipitate weights (mg) Am-241	Ra-226	Th-230	Uranium
1[a]				
2	45.5 ± 1.5	37.7 ± .8	39.8 ± 2.2	44.3 ± 2.5
3	18.5 ± .2[b]	24.3 ± .2	24.2 ± .2	24.5 ± .4
4	22.1 ± 1.4	22.5 ± .6	22.8 ± .6	22.1 ± .3
5	24.4 ± .2	23.9 ± .2	24.5 ± .4	25.9 ± .6
6	22.4 ± .9	24.3 ± .3	23.8 ± .8	22.4 ± .7
7	18.0 ± .7	17.7 ± .2	16.6 ± .7	17.4 ± .4
8	19.3 ± .7	22.6 ± .5	19.9 ± .2	21.5 ± .3
9	23.4 ± 2.5	19.1 ± 1.5	19.5 ± .3	18.0 ± 1.0
10	24.2 ± .3	23.5 ± .2	23.0 ± .2	24.5 ± .8
11	25.1 ± .3	23.7 ± .7	24.2 ± .2	24.1 ± .3
12	23.7 ± .5	23.3 ± 3.3	21.0 ± .8	24.3 ± 1.2
13	26.1 ± .2	25.9 ± .5	25.0 ± .2	26.8 ± .5
14	40.6 ± .8	46.3 ± .5	41.7 ± .6	47.3 ± 1.0
15	24.3 ± .4	24.2 ± .3	24.4 ± .4	24.7 ± .5
16	19.6 ± .3	21.3 ± 1.7	21.9 ± 1.1	24.3 ± 1.4
17	23.3 ± .3	23.9 ± 1.0	23.6 ± .6	24.6 ± 1.6
18	24.6 ± 1.5	25.5 ± .2	26.3 ± .7	27.7 ± .3

[a]Lab 1 did not submit coprecipitate weights.
[b]Lab used a membrane filter for Am-241 and a glass fiber filter for the other three standards.

TABLE 2. COPRECIPITATE WEIGHTS FOR WATER SAMPLES

Laboratory	Water sample coprecipitate weights A	B	C	D
1[a]				
2	46.3 ± 1.1	37.7 ± 2.3	38.6 ± .3	37.9 ± .6
3	24.7 ± .6	23.0 ± .0	24.9 ± .4	25.4 ± .9
4	23.0 ± .6	21.4 ± .4	24.5 ± 2.3	21.0 ± .4
5	24.5 ± .0	23.5 ± .6	23.9 ± .3	22.1 ± .1
6	22.6 ± .4	21.7 ± 1.9	22.7 ± .7	22.4 ± .4
7	17.4 ± .2	17.4 ± .3	18.5 ± .4	18.4 ± .1
8	18.1 ± .5	21.3 ± .4	19.3 ± .5	21.3 ± 1.1
9	19.8 ± .6	18.6 ± 1.0	22.2 ± .5	21.9 ± .7
10	25.5 ± .9	23.2 ± .5	24.1 ± .6	25.1 ± .1
11	24.3 ± 1.2	24.5 ± 1.0	24.5 ± .4	24.0 ± .3
12	20.0 ± .0	23.0 ± .0	19.0 ± .0	23.0 ± .0
13	26.3 ± .7	26.8 ± .4	26.4 ± .8	26.5 ± .5
14	44.2 ± .6	45.8 ± .2	45.0 ± .6	44.1 ± .2
15	22.5 ± .2	24.5 ± .1	24.2 ± .2	24.1 ± .2
16	24.3 ± .4	23.8 ± .3	23.7 ± .5	24.7 ± .4
17	26.0 ± 1.0	25.7 ± .6	26.5 ± .8	26.6 ± 1.0
18	27.1 ± .5	28.4 ± 1.5	28.8 ± 1.2	26.4 ± .8

[a]Lab 1 did not submit coprecipitate weights.

TABLE 3. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE A

Laboratory	Using four standard efficiency factors gross alpha activity, pCi/L±2S			
	Am-241	Ra-226	Th-230	Uranium
1	73.45 ± 5.0	60.4 ± 6.2	101.0 ± 7.4	126.0 ± 9.0[a]
2	45.2 ± 5.6	72.7 ± 10.8	69.9 ± 9.4	80.3 ± 5.4
3	50.7 ± 5.0	46.3 ± 4.0	67.0 ± 5.8	72.0 ± 5.8
4	39.5 ± 2.6	58.5 ± 4.0	56.2 ± 3.8	61.8 ± 4.0
5	54.5 ± 19.8	78.3 ± 28.4	85.2 ± 30.8	108 ± 39.2
6	39.0 ± 2.2	54.7 ± 3.0	63.2 ± 3.4	64.9 ± 3.6
7	79.0 ± 7.2	90.8 ± 8.2	93.8 ± 8.4	92.5 ± 8.4
8	45.0 ± 4.2	53.7 ± 5.0	55.0 ± 5.2	82.5 ± 7.8
9	62.5 ± 4.8	77.3 ± 6.0	75.9 ± 5.8	80.0 ± 6.1
10	42.5 ± 6.2	50.6 ± 7.4	54.2 ± 8.0	69.6 ± 10.2
11	41.3 ± 6.4	57.1 ± 8.8	57.3 ± 9.0	60.9 ± 9.4
12	50.1 ± 6.2	74.0 ± 6.0	76.4 ± 9.6	66.9 ± 8.2
13	40.9 ± 2.8	69.3 ± 4.6	60.9 ± 4.0	62.5 ± 4.2
14	44.7 ± 8.2	62.0 ± 10.6	64.0 ± 10.6	77.3 ± 13.2
15	55.8 ± 6.4	64.6 ± 7.4	65.2 ± 7.6	71.6 ± 15.8
16	42.2 ± 8.0	59.1 ± 11.2	56.5 ± 10.8	69.6 ± 13.2
17	51.9 ± 3.2	48.8 ± .34	62.1 ± 3.8	61.3 ± 3.6
18	32.7 ± 8.4	50.6 ± 13.0	59.6 ± 15.4	71.5 ± 18.6
$X \pm S_n$	49.5 ± 11.7	62.7 ± 11.7	68.0 ± 13.2	73.7 ± 12.0
S_{n-1}	12.1	12.1	13.6	12.4

Known value for gross alpha early count was 74.0 ± 3.7 pCi/L.

[a]T-test indicated result was an outlier; therefore, the result was not used for grand average calculation.

TABLE 4. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE B

Laboratory	Using four standard efficiency factors gross alpha activity, pCi/L±2S			
	Am-241	Ra-226	Th-230	Uranium
1	46.1 ± 5.6	37.6 ± 4.6	63.7 ± 7.8	79.0 ± 9.8
2	30.0 ± 6.2	48.2 ± 9.2	46.3 ± 9.0	53.6 ± 14.2
3	39.3 ± 1.0	36.3 ± 1.0	52.3 ± 1.0	56.3 ± 1.0
4	33.5 ± 3.0	49.6 ± 4.4	47.7 ± 4.2	52.5 ± 2.3
5	45.2 ± 16.4	64.9 ± 23.4	70.6 ± 25.6	89.6 ± 32.4
6	31.7 ± 8.6	44.6 ± 12.0	51.5 ± 13.8	52.9 ± 14.2
7	54.4 ± 2.0	62.5 ± 2.2	64.6 ± 2.4	63.7 ± 2.2
8	39.1 ± 2.8	46.6 ± 3.2	47.8 ± 3.4	71.7 ± 5.0
9	46.7 ± 1.8	57.9 ± 2.4	56.8 ± 2.2	59.9 ± 2.4
10	34.0 ± 1.4	40.5 ± 1.8	43.4 ± 1.8	55.7 ± 2.4
11	35.0 ± 4.0	48.4 ± 5.4	48.6 ± 5.4	51.6 ± 5.8
12	43.5 ± 4.2	59.8 ± 0.6	66.3 ± 6.4	58.0 ± 5.6
13	34.1 ± 2.8	57.9 ± 4.6	50.9 ± 4.2	52.3 ± 4.2
14	32.0 ± 4.4	44.0 ± 5.6	46.0 ± 5.6	55.3 ± 6.6
15	40.4 ± 6.6	46.8 ± 7.6	47.2 ± 7.8	52.1 ± 8.6
16	33.5 ± 1.0	46.9 ± 1.4	44.8 ± 1.2	55.2 ± 1.6
17	40.5 ± 1.4	40.2 ± 0.4	48.5 ± 1.6	47.8 ± 1.6
18	24.5 ± 1.4	37.9 ± 2.0	44.7 ± 2.4	53.6 ± 2.8
$X \pm S_n$	38.0 ± 7.1	48.4 ± 8.6	52.3 ± 8.2	58.9 ± 10.5
S_{n-1}	7.3	8.8	8.4	10.8

Known value for gross alpha early count was 52.6 ± 2.6 pCi/L.

TABLE 5. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE C

Laboratory	Using four standard efficiency factors gross alpha activity, pCi/L±2S			
	Am-241	Ra-226	Th-230	Uranium
1	5.2 ± .40	4.2 ± .34	7.2 ± .58	8.9 ± .72
2	4.24 ± 1.30	6.83 ± 2.26	6.57 ± 2.04	7.53 ± 1.86
3	5.40 ± .58	4.93 ± .50	7.13 ± .76	7.63 ± .76
4	3.63 ± .40	5.37 ± .50	5.17 ± .50	5.67 ± .50
5	11.9 ± 2.8[a]	17.0 ± 4.0[a]	18.5 ± 4.4[a]	23.5 ± 5.6[a]
6	4.43 ± .24	6.22 ± .36	7.19 ± .40	7.38 ± .44
7	5.83 ± .58	6.71 ± .66	6.93 ± .70	6.83 ± .68
8	4.09 ± 1.12	4.88 ± 1.34	5.00 ± 1.36	7.50 ± 2.06
9	3.97 ± .44	4.92 ± .54	4.83 ± .52	5.09 ± .56
10	3.99 ± .60	4.76 ± .72	5.10 ± .78	6.54 ± 1.0
11	3.56 ± 1.16	4.92 ± 1.62	4.94 ± 1.62	5.24 ± 1.72
12	4.57 ± .68	6.30 ± .48	6.97 ± 1.10	6.07 ± 1.0
13	3.72 ± .64	6.30 ± 1.10	5.54 ± .96	5.69 ± .98
14	4.67 ± .94	6.00 ± 1.64	6.67 ± .94	7.67 ± .94
15	5.22 ± .58	6.02 ± .66	6.08 ± .66	6.67 ± .76
16	4.39 ± 1.14	6.14 ± 1.58	5.87 ± 1.52	7.23 ± 1.86
17	3.93 ± .38	3.60 ± .32	4.67 ± .46	4.60 ± .56
18	2.17 ± .44	3.36 ± .68	3.96 ± .80	4.76 ± .96
$X \pm S_n$	4.29 ± .83	5.38 ± 1.01	5.87 ± 1.02	6.53 ± 1.18
S_{n-1}	0.85	1.05	1.05	1.21

Known value for gross alpha early count was 4.8 ± .24 pCi/L.

[a]Data not used for determining grand average; failed the t-test.

TABLE 6. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE D

	Using four standard efficiency factors gross alpha activity, pCi/L±2S			
Laboratory	Am-241	Ra-226	Th-230	Uranium
1	6.10 ± .66	4.96 ± .54	8.40 ± .90	10.4 ± 1.12
2	6.49 ± 1.66	10.45 ± 2.92	10.05 ± 2.74	11.52 ± 2.24
3	7.37 ± .68	6.77 ± .68	9.73 ± .92	10.50 ± 1.02
4	6.13 ± .40	9.07 ± .66	8.70 ± .58	9.57 ± .66
5	5.05 ± .56	7.26 ± .80	7.90 ± .88	10.02 ± 1.12
6	4.99 ± .74	7.00 ± 1.04	8.10 ± 1.22	8.31 ± 1.24
7	10.6 ± .50	12.1 ± .58	12.5 ± .60	12.4 ± .58
8	7.62 ± .58	9.10 ± .68	9.31 ± .70	14.0 ± 1.06
9	9.72 ± 1.08	12.03 ± 1.24	11.81 ± 1.32	12.45 ± 1.38
10	6.11 ± .82	7.27 ± .96	7.79 ± 1.06	10.0 ± 1.34
11	7.75 ± 2.16	10.7 ± 3.0	10.7 ± 3.0	11.4 ± 3.2
12	8.53 ± 1.82	11.7 ± 1.48	13.0 ± 2.60	11.4 ± 2.40
13	6.51 ± .86	11.03 ± 1.44	9.70 ± 1.26	9.96 ± 1.30
14	7.0 ± 0.0	9.0 ± 0.0	9.33 ± .94	11.33 ± .94
15	8.31 ± 1.10	9.61 ± 1.26	9.70 ± 1.28	10.7 ± 1.40
16	5.80 ± 1.80	8.12 ± 2.50	7.77 ± 2.40	9.56 ± 2.96
17	6.83 ± .62	6.37 ± .80	8.17 ± .80	8.03 ± .76
18	4.13 ± 1.62	6.39 ± 2.50	7.53 ± 2.96	9.03 ± 3.56
$X \pm S_n$	6.95 ± 1.60	8.83 ± 2.12	9.45 ± 1.61	10.50 ± 1.46
S_{n-1}	1.64	2.18	1.65	1.50

Known value for gross alpha early count was 10.0 pCi/L (± .5).

TABLE 7. SAMPLE RADIONUCLIDE CONTENT AND GROSS ALPHA GRAND AVERAGES

Sample Spike Concentrations		Gross Alpha pCi/L[a]			
		Am-241	Ra-226	Th-230	Uranium
Sample A					
Ra-226	47.2 pCi/L	49.5 ± 11.7	62.7 ± 11.7	68.0 ± 13.2	73.7 ± 12.0
Po-210	24.1 pCi/L				
[b]Gross Alpha	74.0 pCi/L				
Sample B					
Ra-226	20.5 pCi/L	38.0 ± 7.1	48.4 ± 8.6	52.3 ± 8.2	58.9 ± 10.5
Po-210	10.4 pCi/L				
Uranium	20.5 pCi/L				
[b]Gross Alpha	52.6 pCi/L				
Sample C					
Ra-226	3.0 pCi/L	4.29 ± .83	5.38 ± 1.01	5.87 ± 1.02	6.53 ± 1.18
Po-210	1.5 pCi/L				
[b]Gross Alpha	4.8 pCi/L				
Sample D					
Uranium	10.0 pCi/L	6.95 ± 1.60	8.83 ± 2.12	9.45 ± 1.61	10.59 ± 1.46
[b]Gross Alpha	10.0 pCi/L				

[a]Gross alpha activity values for each sample as determined with the four standard counting efficiencies.
[b]Gross alpha activity at three hours after separation.

TABLE 8. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE A
PRECISION, ACCURACY AND BIAS SUMMARY

Paramter [a]	Sample A, pCi/L using various standard efficiency factors Am-241	Ra-226	Th-230	Uranium
Y_j(pCi/L)	74.0 ± 3.7	74.0 ± 3.7	74.0 ± 3.7	74.0 ± 3.7
$\bar{X}_j$(pCi/L)	49.5	62.7	68.0	73.7
A_j(%)	66.9	84.7	91.9	99.6
Bias (%)[b]	-33.1	-15.3	-8.1	-0.40
$S_{\bar{X}j}$(pCi/L)	11.7	11.7	13.2	12.0
S_{rj}(pCi/L)	3.5	5.0	5.4	6.7
S_{Lj}(pCi/L)	11.5	11.3	12.8	11.3
S_{Rj}(pCi/L)	12.0	12.3	13.9	13.1
V_{rj}(%)	7.1	8.0	7.9	9.1
V_{Lj}(%)	23.2	18.0	18.8	15.3
V_{Rj}(%)	24.2	19.6	20.4	17.8
T_j[c]	8.88	4.09	1.93	0.10

[a]Parameters are described in text.
[b]The sign before the number indicates the direction of bias.
[c]The critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

TABLE 9. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE B PRECISION, ACCURACY, AND BIAS SUMMARY

Paramter [a]	Sample B, pCi/L using various standard efficiency factors Am-241	Ra-226	Th-230	Uranium
Y_j(pCi/L)	52.6 ± 2.6	52.6 ± 2.6	52.6 ± 2.6	52.6 ± 2.6
$\bar{X}_j$(pCi/L)	38.0	48.4	52.3	58.9
A_j(%)	72.2	92.0	99.4	112.0
Bias (%)[b]	-27.7	-8.0	-0.6	+12.0
$S_{\bar{X}j}$(pCi/L)	7.1	8.6	8.2	10.5
S_{rj}(pCi/L)	2.8	3.7	4.1	5.0
S_{Lj}(pCi/L)	6.9	8.3	7.8	10.1
S_{Rj}(pCi/L)	7.4	9.1	8.8	11.3
V_{rj}(%)	7.4	7.6	7.8	8.5
V_{Lj}(%)	18.1	17.1	14.9	17.1
V_{Rj}(%)	19.5	18.8	16.8	19.2
T_j[c]	8.74	2.07	0.15	2.54

[a]Parameters are described in text.
[b]The sign before the number indicates the direction of bias.
[c]The critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

TABLE 10. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE C PRECISION, ACCURACY, AND BIAS SUMMARY

Paramter [a]	Sample C, pCi/L using various standard efficiency factors Am-241	Ra-226	Th-230	Uranium
Y_j(pCi/L)	4.8 ± .24	4.8 ± .24	4.8 ± .24	4.8 ± .24
X_j(pCi/L)	4.29	5.38	5.87	6.53
A_j(%)	89.4	112.0	122.0	136.0
Bias (%)[b]	-10.6	+12.1	+22.3	+36.0
S_{Xj}(pCi/L)	0.83	1.01	1.02	1.18
S_{rj}(pCi/L)	0.37	0.53	0.51	0.57
S_{Lj}(pCi/L)	0.81	0.96	0.98	1.13
S_{Rj}(pCi/L)	0.89	1.10	1.10	1.26
V_{rj}(%)	3.6	9.8	8.7	8.7
V_{Lj}(%)	18.9	17.8	16.7	17.3
V_{Rj}(%)	20.7	20.4	18.7	19.3
T_j[c]	2.55	2.42	4.32	6.04

[a]Parameters are described in text.
[b]The sign before the number indicates the direction of bias.
[c]The critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

TABLE 11. GROSS ALPHA PARTICLE ACTIVITY IN WATER SAMPLE D PRECISION, ACCURACY, AND BIAS SUMMARY

Paramter [a]	Sample D, pCi/L using various standard efficiency factors Am-241	Ra-226	Th-230	Uranium
Y_j(pCi/L)	10.0 ± .5	10.0 ± .5	10.0 ± .5	10.0 ± .5
$\bar{X}_j$(pCi/L)	6.95	8.83	9.45	10.59
A_j(%)	69.54	88.3	94.5	106.0
Bias (%)[b]	-30.5	-11.7	-5.5	+6.0
$S_{\bar{X}j}$(pCi/L)	1.60	2.12	1.61	1.46
S_{rj}(pCi/L)	0.57	0.77	0.83	0.90
S_{Lj}(pCi/L)	1.56	2.07	1.54	1.36
S_{Rj}(pCi/L)	1.66	2.21	1.75	1.63
V_{rj}(%)	8.2	8.7	8.8	8.5
V_{Lj}(%)	22.4	23.4	16.3	12.8
V_{Rj}(%)	23.9	25.0	18.5	15.4
T_j[c]	8.03	2.34	1.45	1.73

[a]Parameters are described in text.
[b]The sign before the number indicates the direction of bias.
[c]The critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

TABLE 12. ESTIMATED RADIUM-226 IN WATER SAMPLES

Labaoratory	CPM/pCi	Estimated Ra-226, pCi/L			
		Sample A	Sample B	Sample C	Sample D
1	0.8312	46.9 ± 4.1	23.3 ± 2.5	2.9 ± .52	0.0
2	0.1540	47.7 ± 3.7	21.1 ± 4.0	3.9 ± .75	0.0
3	0.5392	44.8 ± 2.3	21.0 ± .3	3.1 ± .28	0.0
4	0.3984	43.3 ± .9	19.7 ± .9	2.8 ± .25	0.0
5	0.4241	39.4 ± 4.2	13.1 ± 3.2		
6	0.4084	50.9 ± .9	17.7 ± 2.6	2.1 ± .18	0.8
7	0.7089	46.2 ± 1.8	20.8 ± 1.4	3.3 ± .43	0.0
8	0.5367	46.7 ± 2.7	25.9 ± 2.8	3.0 ± .71	0.0
9	0.7264	49.3 ± 2.3	22.6 ± 1.6	3.7 ± .33	0.0
10	0.4074	45.8 ± 3.7	21.1 ± 1.0	2.6 ± .44	0.0
11	0.3682	46.9 ± 5.6	21.1 ± 1.7	2.5 ± .42	0.0
12	0.4361	31.7 ± 2.0	11.2 ± 1.3	2.5 ± .35	0.0
13	0.3729	51.8 ± 2.1	22.5 ± 1.6	3.0 ± .52	0.0
14	0.5222	50.5 ± 3.3	19.6 ± .9	2.0 ± .53	0.0
15	0.6944	45.3 ± 2.6	36.3 ± 2.6	3.0 ± .27	0.0
16	0.2646	74.9 ± 4.2	15.2 ± .7	3.9 ± .46	0.0
17	0.7289	31.9 ± .8	22.1 ± 1.2	2.1 ± .13	0.0
18	0.2741	41.7 ± 9.8	22.1 ± 1.4	2.3 ± .20	0.0
Average		46.4 ± 8.8	20.9 ± 5.1	2.9 ± 0.6	0.0
Known Value		47.2	20.5	3.0	0.0

TABLE 13. ESTIMATED RADIUM-226 IN WATER SAMPLES

Labaoratory	Efficiency[a] Cpm/pCi	Estimated Ra-226, pCi/L			
		Sample A	Sample B	Sample C	Sample D
1	0.8595 ± .0604	45.4	22.5	3.8	0.0
2	0.1722 ± .0215	42.7	18.8	3.5	0.0
3	0.5389 ± .0193	44.8	21.0	3.1	0.0
4	0.3760 ± .0072	45.9	20.8	3.0	0.0
5	0.3129 ± .0411	53.4	17.8		0.0
6	0.3580 ± .0656	58.1	20.2	2.3	0.0
7	0.7346 ± .0420	44.6	20.3	3.2	0.0
8	0.5828 ± .0668	43.0	23.8	2.8	0.0
9	0.8190 ± .0591	43.7	20.0	3.3	0.0
10	0.3901 ± .0260	47.8	22.0	2.7	0.0
11	0.3499 ± .0335	49.4	22.3	2.6	0.0
12	0.2992 ± .0528	46.2	16.3	3.7	0.0
13	0.3974 ± .0195	48.6	21.1	2.8	0.0
14	0.4702 ± .0873	56.1	21.8	2.2	<1
15	0.6970 ± .0277	45.2	21.6	3.0	0.0
16	0.4123 ± .0495	48.1	23.3	2.5	0.0
17	0.5105 ± .0203	45.6	21.6	2.9	0.0
18	0.2503 ± .0338	45.6	24.2	2.6	0
Average		47.4 ± 4.2	21.1 ± 1.8	2.9 ± .4	0.0
Known Value		47.2	20.5	3.0	0.0

[a]Average efficiency calculated for Samples A, B, and C by using the known values (pCi/L) and the participant laboratory cpm.

TABLE 14. ESTIMATED RADIUM-226 IN WATER SAMPLES

Labaoratory	Cpm/pCi	Estimated Ra-226, pCi/L			
		Sample A	Sample B	Sample C	Sample D
1	0.8181	48.1	23.9	3.0	0.0
2	0.1553	47.3	20.9	3.9	0.0
3	0.5574	43.3	20.3	3.0	0.0
4	0.4072	42.4	19.3	2.8	0.0
5	0.4230	39.5	13.2		0.0
6	0.4090	49.8	16.7	1.9	0.0
7	0.6693	44.0	18.5	3.2	0.0
8	0.5309	47.4	26.1	3.1	0.0
9	0.7139	50.1	22.9	3.8	0.0
10	0.4075	45.8	21.1	2.6	0.0
11	0.3824	45.2	20.4	2.4	0.0
12	0.4294	32.2	11.4	2.6	0.0
13	0.3936	49.1	21.3	2.8	0.0
14	0.5269	50.0	19.5	2.0	0.0
15	0.6851	45.9	21.9	3.0	0.0
16	0.2668	74.3	36.0	3.9	0.0
17	0.7385	31.5	15.0	2.0	0.0
18	0.2697	42.3	22.4	2.4	0.0
Average		46.0 ± 8.6	20.6 ± 5.2	2.85 ± .60	0.0
Known Value		47.2	20.5	3.0	0.0

TABLE 15. ESTIMATED RADIUM-226 IN WATER SAMPLES

Labaoratory	Cpm/pCi	Estimated Ra-226, pCi/L			
		Sample A	Sample B	Sample C	Sample D
1	0.7564 ± .0364	51.6	25.6	3.2	0.0
2	0.1724 ± .020	42.6	18.8	3.5	0.0
3	0.5410 ± .0147	44.6	20.9	3.1	0.0
4	0.3722 ± .0009	46.4	21.1	3.0	0.0
5	0.3227 ± .0234	51.8	17.3		0.0
6	0.3551 ± .0727	57.4	19.2	2.2	0.0
7	0.7532 ± .0501	39.1	16.4	2.8	0.0
8	0.5734 ± .0638	43.9	24.2	2.8	0.0
9	0.8100 ± .0662	44.2	20.2	3.3	0.0
10	0.3919 ± .0264	47.6	21.9	2.7	0.0
11	0.3573 ± .0338	48.3	21.8	2.5	0.0
12	0.3056 ± .060	45.3	16.0	3.6	0.0
13	0.3942 ± .0194	49.0	21.3	2.8	0.0
14	0.4685 ± .0952	56.3	21.9	2.2	0.0
15	0.6872 ± .0270	45.8	21.9	3.0	0.0
16	0.4113 ± .0535	48.2	23.4	2.5	0.0
17	0.5082 ± .0168	45.8	21.7	2.9	0.0
18	0.2496 ± .0334	45.7	24.2	2.6	0.0
				(2.86)	
Average		47.4 ± 4.4	21.0 ± 2.6	2.9 ± .04	0.0
Known Value		47.2	20.5	3.0	0.0

TABLE 16. ESTIMATED RADIUM-226 IN WATER SAMPLES PRECISION, ACCURACY, AND BIAS SUMMARY

Paramter[a]	Water Samples[b] A	B	C	D
Y_j(pCi/L)	47.2 ± 2.4	20.5 ± 1.0	3.0 ± .1	0.0
$\overline{X}_j$(pCi/L)	46.4	20.9	2.9	0.0
A_j(%)	98.3	102.	96.7	
Bias (%)[b]	-1.7	+1.9	-3.3	
$S_{\overline{X}j}$(pCi/L)	8.8	5.1	0.6	
S_{rj}(pCi/L)	3.8	2.0	0.43	
S_{Lj}(pCi/L)	8.7	5.0	0.55	
S_{Rj}(pCi/L)	9.5	5.4	0.69	
V_{rj}(%)	8.2	9.5	14.8	
V_{Lj}(%)	18.7	23.9	19.0	
V_{Rj}(%)	20.5	25.8	23.8	
T_j^c	0.39	0.33	0.71	

[a]Parameters are described in text.
[b]See the text for water sample radionuclide content.
[c]The sign before the number indicates the direction of the bias.
[d]The critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level. The t_c for 17 labs (sample C) is 2.12.

REFERENCES

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American Society for Testing and Materials, "Standard Recommended Practice for Dealing with Outlying Observations," 1981 Annual Book of ASTM Standards, Part 41, Designation: E178-80 ASTM, Philadelphia, Pennsylvania, (1981).

American Society for Testing and Materials, "Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods," 1981 Annual Book of ASTM Standards, Part 41, Designation: E691-79 ASTM, Philadelphia, Pennsylvania, (1981).

Kirby, H. W., "Decay and Growth Tables for the Naturally Occurring Radioactive Serices," AEC Research and Devleopment Report MLM-2042, Atomic Energy Commission, Miamisburg, Ohio, (1973).

Kreiger, H. L., "Interim Radiochemical Methodology for Drinking Water," EPA-600/4-75-008 (Revised), U.S. Environmental Protection Agency, Cincinnati, Ohio, (1976).

Kreiger, H. L., and E. L. Whittaker, "Prescribed Procedures for the Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032, U.S. Environmental Protection Agency, Cincinnati, Ohio, (1980).

Youden, W. J. and E. A. Steiner, "Statistical Manual of the Association of Official Analytical Chemists," Association of Official Analytical Chemists, Washington, D.C., (1975).

APPENDIX A

PARTICIPANT LABBORATORIES

(NOT LISTED IN ORDER OF TABLE LABORATORY NUBMERING)

New Jersey Bureau of Environmental Laboratories
Trenton, New Jersey

Eberline Analytical Corporation
Albuquerque, New Mexico

Arkansas Department of Health
Little Rock, Arkansas

Environmental Resources Center
Georgia Institute of Technology
Atlanta, Georgia

Virginia Radiological Health Laboratory
Richmond, Virginia

State Laboratory of Hygiene
Madison, Wisconsin

Maine Public Health Laboratory
Augusta, Maine

Texas Health Department
Austin, Texas

Orlando Laboratories
Orlando, Florida

Connecticut Department of Health Services
Hartford, Connecticut

New Mexico Scientific Laboratory Division
Albuquerque, New Mexico

Michigan Department of Public Health
Radiological Health Lab
Lansing, Michigan

St. Louis County Health Department
Clayton, Missouri

Westinghouse Advanced Energy Systems Division
Waltz Mill Site
Madison, Pennsylvania

Utah State Health Department
Salt Lake City, Utah

Mississippi State Department of Health
Radiological Health Lab
Jackson, Mississippi

Tennessee Division of Laboratory Services
Nashville, Tennessee

Oak Ridge Assoicated Universities
Low Level Laboratory
Oak Ridge, Tennessee

APPENDIX B

ANALYTICAL TEST PROCEDURE

Determination of Gross Alpha Activity in Drinking Water by Coprecipitation

1.0 Scope and Application

1.1 Many drinking water supplies contain dissolved solids at such high concentrations (>500 mg/liter) that measurement of gross alpha activity by evaporating an aliquot of a sample and counting for alpha activity seriously lacks sensitivity and reproducibility. The nitrated salts (formed by evaporation of a sample aliquot containing nitric acid) of some water samples are hygroscopic and must be converted to the oxides by heating to get a stable sample residue.

1.2 This method provides for the separation of all actinide alpha emitting radionuclides by coprecipitation with barium sulfate and iron hydroxide from liter samples of drinking water. Dissolved solids problems are elminiated. Sensitivity can be increased by using larger sample aliquots. Reproducibility is improved by the use of constant amounts of carrier (barium and iron).

1.3 This method provides for a screening measurement to indicate whether specific radium-226 or uranium analysis or both are required for a drinking water supply.

2.0 Summary of Method

2.1 An aliquot of a drinking water sample is acidified with sulfuric acid and is boiled vigorously for 10 minutes to outgas carbon dioxide and radon-222 from the sample. Barium carrier is added, and the aliquot is stirred for about 30 minutes to coprecipitate radium with barium sulfate.

2.2 Iron carrier is then added to the aliquot and is then neutralized with ammonium hydroxide; it is continuously heated and stirred for another 30 minutes to coprecipitate other alpha emitters with the iron hydroxide carrier.

2.3 The coprecipitate is filtered, dried, and counted for alpha activity.

3.0 Sampling Handling and Preservation

3.1 A representative sample must be collected from a free-flowing source of drinking water; it should be large enough so that meaningful aliquots can be taken. Contamination from the collection system should be avoided by assuring that no contact occurs between the tap and the mouth of the container.

3.2 To minimize adsorption losses to the walls of the sample container, it is recommeded that samples be preserved at the time of collection by the addition of 5 ml of 70 percent HNO_3 (concentrated) per liter of sample to make the samples 0.35 percent HNO_3 solutions. Samples can be acid-preserved when they arrive at the laboratory. They should then be stored (after acid addition) for at least 16 hours (overnight) before aliquots are taken for analysis.

4.0 Interferences

4.1 Since gross alpha screening of drinking water samples is primarily addressing radium concentrations (especially radium-226) and since the radium isotopes decay to short lived progeny, standards, and samples should be counted at as nearly the same elapsed time as possible after alpha activity precipitation. If there are wide differences in the elapsed time as possible after alpha activity precipitation. If there are wide differences in the elapsed times for standards and for samples in the elapsed time range of 0-20 days, there will be signficant errors in the counting efficiencies used. It is recommeded that a short time be allowed between the alpha activity precipitation and the mid-point of the alpha count. However, three hours should be allowed for the decay of the radon-222 progeny before starting the alpha count.

4.2 Samples that contain sulfate or hydroxide or both insoluble precipitates will have greater total precipitates than from the added barium and iron carriers, and, therefore, will have counting efficiencies that are biased low.

4.3 Iron hydroxide precipitate collected on membrane filters without a holding agent will flake when dried and will easily separate from the filter. Five mg of paper pulp fiber added to the sample will greatly help to secure the iron hydroxide to the filter. Glass fiber filters are recommended instead of membrane filters because the surface glass fibers also help to secure the precipitate to the filter.

5.0 Appartus

5.1 Hotplate/magnetic stirrer and stirring bars.

5.2 Glassware.

5.3 Filter membranes, 47 mm diameter, 0.45 micrometer pore size or glass fiber filters, such as Gelman Type A/E or Millipore Type AP.

5.4 Drying lamp.

5.5 Planchets, stainless steel, 2-inch diameter.

5.6 Alpha scintillation counter or low background proportional alpha counter.

6.0 Reagent

6.1 Ammonium hydroxide, 6M. Dilute 400 ml reagent grade NH_4OH to 1 liter with distilled water.

6.2 Barium carrier, 5 mg Ba^{+2}m/l. Dissolve 4.4 g $BaCl_2.9H_2O$ in 500 ml distilled water.

6.3 Bromocersol purple, 0.1 percent. Dissolve 100 mg of the water soluble reagent in 100 ml distilled water.

6.4 Iron carrier, 5 mg Fe^{+3}/ml. Dissolve 17.5 g $Fe(NO_3)_3 \cdot 9H_2)$ in 200 ml distilled water containing 2 ml 16M HNO_3. Dilute to 500 ml.

6.5 Sulfuric acid, 1M. Dilute 55 ml of the 96 percent reagent grade H_2SO_4 to 1 liter with distilled water.

6.6 Paper pulp/water mixture - add a 0.5 g paper pulp pellet to 500 ml of distilled water plus 5 drops of a (1+4) detergent plus water solution in a plastic bottle. Cap the bottle and stir vigorously for three hours before using. This mixture should be stirring when an aliquot is taken.

6.7 Five drops of a (1+4) detergent plus water solution added to the sample will prevent the precipitate from collecting on the beaker wall and will assist in filtering the precipitate. (Examples of wetting agents: Rohm and Haas Triton N101 or Triton X100).

7.0 Calibration

7.1 Thorium-230 is a recommeded pure alpha emitter for gross alpha efficiency calibration especially if the alpha contribution to the beta channel is to be determined. If only gross alpha measurements are to be made on samples, natural uranium is an adequate standard for gross alpha counting efficiency calibration.

7.2 Spike 500 ml portions of tap water in separate beakers (at least 100 pCi) of standard alpha emitter activity. Add 2.5 ml of HNO_3 (Conc.) to each spiked sample. With these spiked samples, determine a counting efficiency (cpm/pCi) for the alpha emitter by taking the samples through the procedure (parts 8.1 - 8.10).

7.3 Unspiked tap water portions (500 ml) should be taken through the procedure for blank corrections of alpha activity in the tap water plus the reagent used.

7.4 Calculations

$$\text{Efficiency, cpm/pCi} = \frac{C_s - C_b}{\text{pCi}}$$

C_s = mean spiked sample counts per minute
C_b = mean blank counts per minute
pCi = spike activity

8.0 Procedure (the following method was presented by Robert Lieberman of the Eastern Environmental Radiation Facility, Montgomery, Alabama, at the Health Physics Society meeting in Las Vegas, Nevada, August, 1982. Some minor changes were made as a result of a single laboratory test of the method by the EMSL-Las Vegas, Quality Assurance Division).

8.1 Use a measured aliquot of water sample. If the sample is less than 500 ml, dilute to 500 ml with distilled water. Samples of 500 ml to 1 liter may be used as is.

8.2 Add 5 drops of the (1+4) detergent plus water reagent.

8.3 Place the sample on a magnetic stirrer/hot plate and, while stirring, gently add 20 ml of 1M H_2SO_4 and boil for 10 minutes to flush carbon dioxide (from carbonates and bicarbonates) from the sample. Radon will also be flushed from the sample.

8.4 Lower the hot plate temperature to below sample boiling, continue stirring, and add 1 ml of barium carrier solution (5 mg Ba/ml). Continue stirring for 30 minutes.

8.5 Add 1 ml of bromocresol purple indicator solution, 1 ml of iron carrier solution, and 5 ml of paper pulp/water regent (aliquot taken while the paper pulp/water mixture is stirring.)

8.6 Continue stirring and add 6M HN_4OH dropwise to the sample until there is a distinct color change (yellow to purple). Continue warming and stirring for 30 minutes.

8.7 Filter the sample through a glass fiber filter (or membrane filter if further analysis is to be done) to rinse all precipitate from the beaker to the filter. Wash the precipitate with 25 ml of distilled water.

8.8 Allow 3 hours for the collected radon progeny to decay and to dry the filter at 105°C or under a mild heat lamp.

8.9 Count the filters for gross alpha activity. An early count of the

gross alpha activity, after the three hour decay period, is recommended to minimize additional radon ingrowth which is not easily corrected for when there are other alpha emitters in the sample.

8.10 Store samples in a desiccator if they are to be recounted at a later date.

8.11 Prepare a reagent blank precipitate to determine the reagent alpha activity background.

9.0 Calculations

9.1 Gross alpha activity, pCi/liter $= \dfrac{C_1 - C_B}{E\ V}$

E = counter efficiency, cpm/pCi
V = volume analyzed, liters.
C_1 = sample, counts per minute
C_B = reagent blank, counts per minute.

9.2 Lower Limit of Detection, LLD

$$\text{LLD, Gross alpha, pCi/liter} = \frac{4.66\ (C_B T)^{1/2}}{E\ V\ T}$$

C_B = reagent background, counts per minute.
T = counting time.
E = counter efficiency, cpm/pCi.
V = reagent blank, counts per minute.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

10.0 Precision and Accuracy

(To be added from single laboratory and multilab tests of the method.)

APPENDIX C

INSTRUCTIONS TO PARTICIPANT LABORATORIES

Contents of Shipment

Before beginning any analytical work, please be sure that you have all of the items listed. If any are missing or broken please call me immediately.

1. Instructions, Appendices A, B, and C, and data report sheets (1-A, 1-B, 2-A, 2-B, and 3)

2. Standard solution concentrates

   a. Ra-226, 30 ml in 50 ml ampul
   b. Th-230, 30 ml in 50 ml ampul
   c. Am-241, 30 ml in 50 ml ampul
   d. Natural Uranium, 30 ml in 50 ml ampul

3. Sample solution concentrates

   a. Sample A concentrate, 30 ml in 50 ml ampul
   b. Sample B concentrate, 30 ml in 50 ml ampul
   c. Sample C concentrate, 30 ml in 50 ml ampul
   d. Sample D concentrate, 30 ml in 50 ml ampul

4. Bromocresol purple indicator solution, 30 ml in 50 ml apmul

5. (1+4) Triton x 100 plus water solution, 30 ml in 50 ml ampul

6. Two each, approximately 0.5 g paper pulp pellets in a small petri dish

Instructions - Multilab Test of the Test Procedure, "Determination of Gross Alpha by Coprecipitation"

Four standard solutions (Ra-226, Th-230, Am-241, and Natural Uranium) are provided with which to determine separate counting efficiencies with spiked samples, coprecipitated with the iron and barium carriers, as describedin the Calibration Section of the Test Procedure. Thirty (30) ml of each standard is provided in the indicated ampuls. Concentrations of the standard solutions are such that 5.0 ml aliquots will give activities in the range of 180 to 300 pCi. Known concentrations of the standard solutions are indicated on the respective ampuls and are listed below.

Ra-226 plus Po-210	186 plus 95.3	pCi./5.00 ml (±3%)
Th-230	285	pCi./5.00 ml (±3%)
Am-241	215	pCi./5.00 ml (±3%)
Natural Uranium	189	pCi./5.00 ml (±3%)

Since the alpha particle activity of the coprecipitated Ra-226 will vary with elapsed time after coprecipitation due to the ingrowth of Rn-222 progeny (see Appendix A), it is important that participants schedule the elapsed time (Δt) between Ra-226 coprecipitation and the alpha activity count (mid-point), the same for the Ra-226 spiked standard samples as they expect to do for the samples to be analyzed by this method. The method calls for an early count after the 3-hour delay (for decay of coprecipiated Ra-226 progeny). In addition, the participants are requested to count the Ra-226 spiked standard samples a second time at a specified Δt of 7 days to measure the progeny ingrown alpha activity. When such two counts are taken of samples of unknown alpha activity, an estimate of the Ra-226 contribution to the sample alpha activity may be made.

Data Report Sheet No. 1A is provided for reporting standard samples data (early count for Ra-226 standard samples). A second Data Report Sheet No. 1B is provided for participants to report the second (Δt = 7 days) count data of the Ra-226 standard samples.

Four sample concentrates (A, B, C and D) are provided which are to be diluted, 5.0 ml of concentrate to 1 liter of your tap water, thus, consituting a 1 liter sample for analysis by the method. Prepare 3 replicate samples (1 liter each) from each concentrate and analyze for gross alpha activity by the method being tested.

Two copies of Report Sheet No. 2 (2A and 2B) are provided so that participants can report two separate alpha counts for each sample, Δt = early count afte separation and Δt = 7 days after separation. The second count is to show which samples contain significant Ra-226 concentrations. However, report the gross alpha activities in pCi/l using the early alpha count data and the 4 different radionuclide standard efficiency factors. Using the early alpha count will minimize the positive bias due to Ra-226 progeny ingrowth.

Please note that the method assumes complete (100 percent) recovery of the alpha emitters by the coprecipitation with barium sulfate and iron hydroxide.

Uranium is not completely recovered by the method. However, by coprecipitating spiked standard samples from diluted solutions as described in the Calibration Section of the method, the counting efficiencies also include recovery factors. All coprecipitate weights should be recorded on the provided data report sheets. These data may be useful in substantiating the consistency of the coprecipitation and/or for normalizing data if significant weight differences are observed. Samples should be alpha counted for at least 30 minutes each.

Appendix C is provide to give instructions for the estimation of the Ra-226 alpha contribution to the gross alpha activity of the samples. Report Sheet

No. 3 is provided for reporting your estimated Ra-226 pCi/l values for each sample.

If you have any questions about the above instructions, please feel free to call me at 702-798-2233 (FTS 545-2233). Please send results by March 1, 1985 to:

Earl Whittaker
EMSL-Las Vegas
P.O. Box 15027
Las Vegas, NV 89114

DATA REPORT SHEET - 1A

Date: _____

Laboratory: _____

Address: _____

_____

Analyst: _____

Telephone: _____

GROSS ALPHA ACTIVITY EFFICIENCY FACTORS AND COPRECIPITATE WEIGHTS

Standard	Efficiency factor Net cpm/pCi	Δ t* (hours)	Counting time (minutes)	Coprecipiate weight (grams)
Am-241	_____		_____	_____
Am-241	_____		_____	_____
Am-241	_____		_____	_____
Ra-226	_____	_____	_____	_____
Ra-226	_____	_____	_____	_____
Ra-226	_____	_____	_____	_____
Th-230	_____		_____	_____
Th-230	_____		_____	_____
Th-230	_____		_____	_____
Uranium	_____		_____	_____
Uranium	_____		_____	_____
Uranium	_____		_____	_____

*Since the elapsed time between radium separation from sample solution and the alpha count is only significant for the Ra-226, Δ t values for only Ra-226 need to be shown.

DATA REPORT SHEET - 1B

Date: _____

Laboratory: _____

Address: _____

_____

Analyst: _____

Telephone: _____

GROSS ALPHA ACTIVITY EFFICIENCY FACTORS AND COPRECIPITATE WEIGHTS

Standard	Efficiency factor Net cpm/pCi	Δ t* (hours)	Counting time (minutes)	Coprecipiate weight (grams)
Am-241	_____		_____	_____
Am-241	_____		_____	_____
Am-241	_____		_____	_____
Ra-226	_____	_____	_____	_____
Ra-226	_____	_____	_____	_____
Ra-226	_____	_____	_____	_____
Th-230	_____		_____	_____
Th-230	_____		_____	_____
Th-230	_____		_____	_____
Uranium	_____		_____	_____
Uranium	_____		_____	_____
Uranium	_____		_____	_____

*Since the elapsed time between radium separation from sample solution and the alpha count is only significant for the Ra-226, Δ t values for only Ra-226 need to be shown.

DATA REPORT SHEET - 2A

Laboratory: _____

TRIPLICATE TEST RESULTS FOR ONE LITER SAMPLE ALIQUOTS

Sample	Δ t (hours)	Counting time (minutes)	Alpha Net cpm	Co-ppt. wt. (grams)	Gross alpha pCi/l using eff. factors			
					Am-241	Ra-226	Th-230	Uranium
A-1								
A-2								
A-3								
B-1								
B-2								
B-3								
C-1								
C-2								
C-3								
D-1								
D-2								
D-3								
Blank-1								
Blank-2								
Blank-3								

DATA REPORT SHEET - 2B

Laboratory: _____

TRIPLICATE TEST RESULTS FOR ONE LITER SAMPLE ALIQUOTS

Sample	Δ t (hours)	Counting time (minutes)	Alpha Net cpm	Co-ppt. wt. (grams)	Gross alpha pCi/l using eff. factors			
					Am-241	Ra-226	Th-230	Uranium
A-1								
A-2								
A-3								
B-1								
B-2								
B-3								
C-1								
C-2								
C-3								
D-1								
D-2								
D-3								
Blank-1								
Blank-2								
Blank-3								

DATA REPORT SHEET NO. 3

Laboratory: _____

ESTIMATED Ra-226 CONCENTRATION (pCi/l)

Sample	Δt = 7 days cpm/l	Early count cpm/l	Early count Δt (hours)	Ra-226 eff.* cpm/pCi	Est. Ra-226 pCi/l
A-1					
A-2					
A-3					
B-1					
B-2					
B-3					
C-1					
C-2					
C-3					
D-1					
D-2					
D-3					

*Use the average of the Δt early count factor and the Δt = 7 days factor. Since the EMSL-Las Vegas Ra-226 standard contains Po-210 (Po-210 to Ra-226 ratio = 0.51), this is a combined efficiency factor.

APPENDIX A

Total alpha factors for radium-226 with change in elapsed time between alpha activity precipitation and the midpoint of the alpha count (from Kriby's tables, "Decay and Growth Tables for the Naturally Occurring Radioactive Series AEC Research and Development Report MLM-2042)."

Elapsed Time Δt = hrs, (days)	Total Alpha Factor Ra-226 Parent Only* Alpha Factor	% Increase	Ra-226 plus Po-210 Fraction** Alpha Factor	% Increase
0	1.0000	0.0	1.5100	0.0
4	1.0800	8.0	1.5900	5.3
8	1.1668	16.7	1.6768	11.0
12	1.2511	25.1	1.7611	16.6
16	1.3329	33.3	1.8429	22.0
20	1.4123	41.2	1.9223	27.3
24 (1)	1.4893	48.9	1.9993	32.4
36	1.7068	70.7	2.2168	46.8
48 (2)	1.9055	90.5	2.4155	60.0
60	2.0870	109	2.5970	72.0
72 (3)	2.2528	125	2.7628	83.0
84	2.4042	140	2.9142	93.0
96 (4)	2.5424	154	3.0524	102
(5)	2.7841	178	3.2941	118
(6)	2.9856	198	3.4956	131
(7)	3.1538	215	3.6638	143
(8)	3.2941	229	3.8041	152
(10)	3.5087	251	4.0187	166
(15)	3.8015	280	4.3115	185
(20)	3.9198	292	4.4298	193
(25)	3.9675	297	4.4775	196
(30)	3.9869	299	4.4969	198

*This data, from Kirby's tables, assumes a pure parent at Δt=0.

**This data is (*) plus a 0.51 fraction of Po-210 which is also an alpha emitter. The ratio of Po-210 to Ra-226 in the EMSL-LV Ra-226 standard (March 23, 1984) is 0.51.

APPENDIX B

Elapsed Time Δt hours	Total alpha	Ingrowth factor	Estimated Ra-226 % bias (-)
0	1.000	0.000	
1	1.016	0.016	
2	1.036	0.036	
3	1.058	0.058	
4	1.080	0.080	3
5	1.102	0.102	4
6	1.124	0.124	5
7	1.145	0.145	6
8	1.166	0.166	7
9	1.188	0.188	8.5
10	1.209	0.209	10
11	1.230	0.230	11
12	1.251	0.251	12
13	1.271	0.271	13
14	1.292	0.292	14
15	1.313	0.313	14.4
16	1.333	0.333	15
17	1.353	0.353	16
18	1.373	0.373	17
19	1.392	0.392	18
20	1.412	0.412	19
21	1.432	0.432	20
22	1.451	0.451	21
23	1.470	0.470	22
24	1.489	0.489	23

APPPENDIX C

Estimation of the Ra-226 alpha contribution to the gross alpha count

The Ra-226 concentration (pCi/l) at $\Delta t = 0$ is estimated by the following equation:

Estimated Ra-226 = Alpha count at Δt = 7 days - Alpha Count at Δt = 0, or early time after separation ÷ counting efficiency (cpm/pCi) x 7 day ingrowth factor* (see Appendices A and B).

*While the total Alpha factor for Ra-226 at 7 days ingrowth time is 3.1538, the alpha ingrowth factor is 3.1538 - 1.000 or 2.1538.

Example:

Assume a sample contains

Ra-226	=	10.0 pCi/l
Po-210	=	5.1 pCi/l
Natural Uranium	=	20.0 pCi/l
Total Alpha	=	35.1 pCi/l at $\Delta t = 0$

Assume counting efficiency = 0.20 cpm/dpm or 0.444 cpm/pCi.

The alpha count at $\Delta t = 0$ would be 0.444 cpm/pCi x 35.1 pCi/l = 15.6 cpm/l.

At 7 days of ingrowth the 10.0 pCi/l Ra-226 alpha component would increase to a total of 10.0 pCi/l x 3.1538 = 31.58 pCi/l.

At Δt = 7 days the total gross alpha would be

Ra-226 plus progency	=	31.58 pCi/l
Po-210	=	5.1 pCi/l
Natural Uranium	=	20.0 pCi/l
		56.6 pCi/l

The Δt = 7 days, alpha count rate would be 0.444 cpm/pCi x 56.5 pCi/l = 25.1 cpm/l

then:

$$\text{Estimated Ra-226} = \frac{25.1 \text{ cpm/l} - 15.6 \text{ cpm/l}}{0.44 \text{ cpm/pCi} \times 2.1538}$$

= 9.93 pCi/l, compared to the 10.0 pCi/l given above.

Since the early alpha count is taken at some time after 3 hours from coprecipitation of the alpha emitters, the estimated Ra-226 component of the sample will be biased low. The percent of bias for early alpha counts of Δt = 4 to 24 hours is shown in Appendix B. Estimated Ra-226 results can be normalized to Δt = 1, using the percent bias values in Appendix B.

In the example above, if the early alpha count had been as late as Δt = 24 hours, the calculations would be as follows:

At Δt = 24 hours the total gross alpha would be:

$$\begin{aligned} \text{Ra-226 plus progeny} &= 10.0 \text{ pCi/l} \times 1.489 = 14.9 \text{ pCi/l} \\ \text{Po-210} &= 5.1 \text{ pCi/l} \\ \text{Natural Uranium} &= 20.0 \text{ pCi/l} \\ &\overline{40.0 \text{ pCi/l}} \end{aligned}$$

and the alpha count would be

$$0.444 \text{ cpm/pCi} \times 40.0 \text{ pCi/l} = 17.8 \text{ cpm/l}$$

$$\text{then the estimated Ra-226} = \frac{25.1 - 17.8}{0.444 \times 2.1538} = 7.63 \text{ pCi/l, which}$$

is biased low by 23 percent.

$$\text{Normalized to } \Delta t = 0, \frac{7.63}{1.0 - 0.23} = 9.92 \text{ pCi/l compared to 10.0 pCi/l.}$$

APPENDIX D

Radium-224 Interference Calculations

Calculations for the Possible Interference of Radium-224 (supported by its parent Th-228) on the Estimation of Radium-226 by an Early and Late Gross Alpha Count of Gross Alpha Activity Coprecipitated with Barium Sulfate and Iron Hydroxide.

From Kirby's tables (Kirby, 1973) of decay and ingrowth factors for the naturally occurring radionuclide series, the following total gross alpha factors are found for the indicated times of pure parent decay.

Pure Parent	Δt	Total Gross Alpha Factor
Ra-226	3 hours	1.0580
Ra-226	7 days	3.1538
Th-228	3 hours	1.0710
Th-228	7 days	3.8861
Ra-224	3 hours	3.0323
Ra-224	5 days	1.6020
Ra-224	7 days	(1.120) estimated value

In the following calculations, it is assumed that Ra-224 is in equilibrium with its parent Th-228 before and after coprecipitation with barium sulfate and iron hydroxide. It is also assumed that the gross alpha counting efficiency is 0.5370 cpm/pCi.

Example 1. When the sample Ra-224 concentration is equal to the sample Ra-226 concentration, and the Ra-224 is in equilibrium with its parent Th-228.

Assume sample radionuclide content to be as follows:

Ra-226	2.05 pCi/L
Po-210	10.4 pCi/L
Ra-228	20.5 pCi/L
Th-228	20.5 pCi/L
Ra-224	20.5 pCi/L

Gross alpha activity at three hours after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 1.0580	=	21.7 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	20.5 pCi/L x 1.0710	=	21.9 pCi/L
Ra-224	20.5 pCi/L x 3.0323	=	62.1 pCi/L
	TOTAL GROSS ALPHA	=	116.1 pCi/L

Gross alpha activity at seven days after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 3.1538	=	64.6 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	20.5 pCi/L x 3.8861	=	79.7 pCi/L
Ra-224	20.5 pCi/L x 1.120	=	22.9 pCi/L
	TOTAL GROSS ALPHA	=	177.6 pCi/L

Then subtracting the early gross alpha count from the late gross alpha count and calculating for the estimated Ra-226 concentration

$$\frac{(177.6 \text{ pCi/L} \times 0.5370 \text{ cpm/pCi}) - (116.1 \text{ pCi/L} \times 0.5370 \text{ cpm/pCi})}{2.1538 \times 0.5370 \text{ cpm/pCi}} = 28.6 \text{ pCi/L}$$

The estimated Ra-226 concentration then would be biased high by

$$\frac{28.6 - 20.5}{20.5} \times 100 = 39.5\%$$

Example 2. When the sample Ra-224 concentration is one half (1/2) the Ra-226 concentration, and the Ra-224 is in equilibrium with its parent Th-228.

Assume sample radionuclide content to be as follows:

Ra-226	20.5 pCi/L
Po-210	10.4 pCi/L
Ra-228	10.2 pCi/L
Th-228	10.2 pCi/L
Ra-224	10.2 pCi/L

Gross alpha activity at three hours after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 1.0580	=	21.7 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	10.4 pCi/L x 1.0710	=	10.9 pCi/L
Ra-224	10.4 pCi/L x 3.0323	=	30.9 pCi/L
	TOTAL GROSS ALPHA	=	73.9 pCi/L

Gross alpha activity at seven days after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 3.1538	=	64.6 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	10.4 pCi/L x 3.8861	=	39.6 pCi/L
Ra-224	10.4 pCi/L x 1.120	=	11.4 pCi/L
	TOTAL GROSS ALPHA	=	126.0 pCi/L

Then subtracting the early gross alpha count from the late gross alpha count and calculating for the estimated Ra-226 concentration

$$\frac{(126.0 \text{ pCi/L} \times 0.5370 \text{ cpm/pCi}) - (73.9 \text{ pCi/L} \times 0.5370 \text{ cpm/pCi})}{2.1538 \times 0.5370 \text{ cpm/pCi}} = 24.2 \text{ pCi/L}$$

The estimated Ra-226 concentration then would be biased high by

$$\frac{24.2 \text{ pCi/L} - 20.5 \text{ pCi/L}}{20.5 \text{ pCi/L}} \times 100 = 18.0\%$$

Example 3. When the sample Ra-224 concentration is two times the Ra-226 concentration, and the Ra-224 is in equilibrium with its parent Th-228.

Assume sample radionuclide content to be as follows:

Ra-226	20.5 pCi/L
Po-210	10.4 pCi/L
Ra-228	41.0 pCi/L
Th-228	41.0 pCi/L
Ra-224	41.0 pCi/L

Gross alpha activity at three hours after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 1.0580	=	21.7 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	10.4 pCi/L x 1.0710	=	43.9 pCi/L
Ra-224	10.4 pCi/L x 3.0323	=	124.3 pCi/L
	TOTAL GROSS ALPHA	=	200.3 pCi/L

Gross alpha activity at seven days after coprecipitation would be as follows:

Ra-226	20.5 pCi/L x 3.1538	=	64.6 pCi/L
Po-210	10.4 pCi/L x 1.000	=	10.4 pCi/L
Th-228	41.0 pCi/L x 3.8861	=	159.3 pCi/L
Ra-224	41.0 pCi/L x 1.120	=	45.9 pCi/L
	TOTAL GROSS ALPHA	=	280.2 pCi/L

Then subtracting the early gross alpha count from the late gross alpha count and calculating for the estimated Ra-226 concentration

$$\frac{(280.2\ \text{pCi/L} \times 0.5370\ \text{cpm/pCi}) - (200.3\ \text{pCi/L} \times 0.5370\ \text{cpm/pCi})}{2.1538 \times 0.5370\ \text{cpm/pCi}} = 37.1\ \text{pCi/L}$$

The estimated Ra-226 concentration then would be biased high by

$$\frac{37.1\ \text{pCi/L} - 20.5\ \text{pCi/L}}{20.5\ \text{pCi/L}} \times 100 = 81.0\%$$